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(71) Applicants: BOLIDEN AKTIEBOLAG; Sturegatan 22, Box 5508, 114 85 Stockholm, Sweden (for all designated States except US). PETERSSON, Stig, Arvid; Vintergatan 25, 932 00 Skelleftehamn, Sweden (for US only). ERIKSSON, Bengt, Sune; Hamnskär, 932 00 Skelleftehamn, Sweden (for US only).

(72) Inventors: PETERSSON, Stig, Arvid; Vintergatan 25, 932 00 Skelleftehamn, Sweden. ERIKSSON, Bengt, Sune; Hamnskär, 932 00 Skelleftehamn, Sweden.

(74) Agent: PENDERUD, Sigvard; Aktiebolaget Fredrik L Enquisits Patentbyrå, P.O. Box 7162, 103 83 Stockholm, Sweden.

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(57) Abstract

A method for the manufacture of an additive material for the production of crude iron which comprises charging an iron sulphidic material to a furnace space together with oxygen and a silicate-containing material in relative proportions such that it is possible to obtain an iron silicate melt containing 60-90 % by weight iron, calculated as iron (II) oxide when melting. The melt is granulated or permitted to solidify and then crushed to pieces of a size suitable to charge to a furnace unit for the production of crude iron.
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A METHOD FOR THE MANUFACTURE OF AN ADDITIVE MATERIAL FOR THE PRODUCTION OF CRUDE IRON

The present invention relates to a method for the manufacture of iron raw material from sulphidic iron-containing materials, preferably pyrite and pyrrhotite.

Pyrite, FeS₂, are mainly used as a sulphur raw material in the production of sulphuric acid and liquid sulphurdioxide, by combusting the sulphur content of the said raw materials with an oxygen-containing gas during a so-called roasting process. During the roasting process, sulphur dioxide is formed and is passed to a plant for the production of sulphuric acid or liquid sulphur dioxide. During the roasting process, the iron content of the pyrite is converted to iron oxides in the form of hematite or magnetite or mixtures thereof, depending upon the roasting method applied. Hitherto, the iron oxides or pyrite cinders have had a low sales value, mainly because they are extremely fine and dust creating and therefore difficult to handle. Further, the quantities in which they are produced are so small, in the order of magnitude of 100,000 tons/year, that it is not sufficiently rewarding for a sintering plant to be erected on the premises of conventional sulphuric acid factory, in which plant the fine-grain material could be converted to agglomerates of the size required for charging to, for example, blast furnaces. Further, the pyrite cinders may be somewhat contaminated with, for example, copper, zink, lead, cobalt, nickel, arsenic, sulphur and noble metals. In the majority of cases the presence of such impurities is not desirable when manufacturing iron and steel. The impurities, primarily copper, zink and arsenic, also render the deposition or dumping of cinders expensive, since it must be ensured that these metals are not leached from the dumping cinders by, for example, rainwater.

For the purpose of reducing the level of impurities in steel, in those cases where pyrite cinders are included as raw
materials, it is common practice to simply dilute the cinders with iron-ore concentrates, which normally do not contain these impurities, although in this case valuable metals such as copper, nickel, cobalt and, in certain cases, also noble metals, cannot be recovered from the cinders.

Consequently, during recent years various processes have been developed which permit the pyrite cinders to be purified and agglomerated, thereby rendering them more suitable as an iron raw-material, whilst at the same time permitting other valuable metals to be recovered. One normal method of procedure in this respect is to treat the cinders with chlorine or a chlorine-containing material, thereby to convert the impurities to chlorides, which, by heating or leaching, can be separated from each other and then recovered. Processes of this type have many disadvantages. Among other things the plants are expensive to operate because of the high investments necessary and because of the considerable quantities of chemicals consumed and the corrosion to which the apparatus are subjected. Further, the use of chlorine incurs costs in the protection of the environment. The viability of said chlorinating refining processes is also dependent upon the presence of relatively large quantities of contaminating and recoverable valuable metals.

The present invention relates to a method of manufacturing an additive material for the production of crude iron and is characterized in that iron-sulphide containing material is charged to a furnace space together with oxygen and silicate-containing material in relative proportions such that subsequent to autogenous smelting taking place there is obtained an iron silicate melt containing approximately 60-90 percent by weight iron, calculated as iron(II)oxide, said melt then being granulated and permitted to solidify, and then crushed to a size suitable for charging to a furnace unit for the production of crude iron.

Thus, the method according to the invention enables pyrite...
to be used directly, not only as a raw material for the production of sulphur dioxide and sulphuric acid, but also as a raw material for the production of iron, by charging pyrite to a smelter, such as a flash smelter, for example a smelter such as that described in US Patent No 3,790,366, together with silica, e.g. quartz sand, and by smelting the pyrites autogenously by charging to the furnace oxygen-gas or oxygen enriched air, thereby to form substantially an iron-silicate melt. When large quantities of non-ferrous metals are present, it is possible in the aforementioned method to ensure that the combustion of sulphur is not carried to completion so that non-ferrous metals having a greater affinity than iron has to sulphur will form a matte, such non-ferrous metals normally being present in pyrite as impurities. The matte is more dense than the oxidic-iron silica melt and is insoluble therein, and hence it can be readily separated and tapped-off separately. The major part of the melt comprising iron oxide-silica, also known as fayalite slag, corresponds approximately to a composition of 2Fe2O3·SiO2, which contains 60–90% iron calculated as iron(II)oxide, is then used as an additive material in the production of iron according to conventional processes and thus comprises a silica and an iron raw material. The excess heat generated when smelting pyrite auto- genously can be utilized to smelt other raw products, such as iron oxides, pyrite cinders, iron-containing slags — e.g. slag obtained from lead and copper smelters — and leaching residues containing substantial quantities of iron.

Smelting to fayalite slag can be effected in a flash smelter, whereafter the resultant fayalite slag is conveniently transferred to moulds and cooled therein. Alternatively the slag can be granulated. The lower limit to which iron can be present in the slag, calculated as iron(II)oxide, is determined by the fact that the melting point rises very quickly when the content of iron is less than 60 percent by weight, while the upper limit is determined by the fact that the amount of iron(III)oxide formed, and therewith the extent to which magnetite is formed, becomes excessively high when the
slag contains more than 90 percent by weight iron, calculated as iron(II) oxide.

When practising the method according to the invention sulphur dioxide and an iron-silica raw material can be produced from pyrite and other iron-sulphidic materials with a relatively small energy consumption and whilst simultaneously recovering other valuable non-ferrous metals. Further, the process enables iron-silicate slag, e.g. slags obtained from lead and copper smelters or plants, to be used as iron raw-materials, since it contains both SiO$_2$ and FeO which are normally present in various crude iron processes.

A further advantage afforded by the process is that fine-grain iron material can be charged to a flash smelter in that state it obtained upon being concentrated, which provides for considerable saving in comparison with, for example, shaft furnaces in which only agglomerated sintered iron raw material can be used.

The method according to the invention also permits the temperatures to be kept relatively low during the process, for example in the range of 1250-1350°C, which is favourable with respect to the furnace lining. When the conditions are such that magnetite is liable to be formed and deposited on the walls of the furnace, the temperature within the furnace should be increased by some hundred degrees.

The method will now be described with reference to a preferred embodiment thereof.

Pyrite and silica are charged to a furnace together with other iron raw materials, such as iron-ore concentrates, fayalite slag obtained from copper and lead plants, or pyrite cinders in the form of hematite or magnetite, in such quantities that a liquid fayalite slag is formed. The furnace is conveniently a flash smelter, although other types of furnaces may be used. Among those furnaces which can be used in
this context ore rotary furnaces and furnaces of a type to which a fine-grain material can be charged and which permit a smelt to be formed. The process may be a continuous process or an intermittent process, depending upon the type of furnace used.

By charging oxygen or air enriched in oxygen to the furnace, the sulphur content and the iron content of the pyrite are combusted suitably in the shaft of a flash smelter, whilst generating large quantities of heat the iron-containing material charged to the furnace being smelted down autogenously and, together with an addition of silica, forms a molten bath comprising mainly a fayalite slag. As beformentioned, ironsulphidic material normally contains non-ferrous metals, such as copper, nickel and cobalt, which form a sulphide phase in which any noble metals present will be refound. The sulphide phase, which is not soluble in the oxidic fayalite slag and which has a higher specific gravity than said slag, is settled on the bottom of the flash smelter and may be tapped therefrom at uniform intervals. Part of the arsenic, antimony and bismuth present will be driven off during the smelting process while the remainder will be dissolved in the sulphide phase.

The fayalite slag is suitably tapped into moulds and allowed to solidify therein, whereafter the solidified mass is crushed to pieces of a size suitable for charging as addition material to raw-iron processes carried out in shaft furnaces, such as blast furnaces. Thus, the process enables the separation and recovery of the non-ferrous metal content of the starting materials, the presence of such non-ferrous metals normally being undesirable in iron products.

Sulphur dioxide containing gas formed during the autogenous smelting process is passed out of the furnace and is suitably led to a plant for the production of sulphuric acid or a plant for the production of liquid sulphur dioxide, subsequent to having been subjected to a heat exchange process.
and cleaned from dust in a conventional manner.

If, when carrying out the method according to the invention, cinders containing Fe(III), obtained from conventional 5 roasting processes, are charged to the furnace, it should be ensured during the smelting process that magnetite is not formed in quantities exceeding approximately 5 percent by weight of the total amount of slag formed. The magnetite has a higher melting point and will impart to the slag a higher viscosity, which renders it difficult to tap-off the slag. By adding coke to the molten bath in the furnace, it is possible to provide reducing conditions which are sufficient to reduce Fe(III) to Fe(II).

15 The combustion of pyrite with air results in a significant excess of heat, which can be utilized to smelt oxidic-iron raw-materials of the type previously mentioned. This excess of heat can be increased considerably by using pre-heated material, air enriched with oxygen or oxygen gas when combusting pyrite.

When 1000 kgs of pyrite is oxidized to form iron(II)oxide and sulphur dioxide the heat of formation will be 2 174 MJ and 4 750 MJ respectively. When adding SiO₂ in quantities such that the compound fayalite (2FeO·SiO₂) is formed, the heat of formation required herefor is only 99 MJ.

The heat of formation liberated by splitting off pyrite (FeS is not included) is 1380 MJ per ton, which provides a net heat development for the process when 100% oxygen gas is used corresponding to 2 174 + 4 750 + 99 - 1 380 MJ, which is equal to 5 643 MJ calculated per ton of pyrite.

The method according to the invention enables pyrite concentrates to be used as raw materials for the recovery of sulphur dioxide and the recovery of iron, since it is possible to produce lumps of iron raw-material suitable charging directly to shaft furnaces, such as blast furnaces. When
carrying out the method, the source of energy comprises mostly the sulphur present in the pyrite concentrates, which sulphur is far less expensive than the higher grade fuels such as coal, oil and gas. A further, significant advantage is that fine-grain iron raw materials can be used.

Iron raw materials containing impurities such as Cu and Pb can be used in known processes only when they have been purified in a special process step or if the impurities are diluted by relatively large quantities of pure iron raw material. In this latter case valuable metals cannot be recovered.
CLAIMS:

1. A method for the manufacture of an addition material for the production of crude iron, characterized in that iron sulphidic material is charged to a furnace space together with oxygen and silicate-containing material in relative proportions such that subsequent to autogenous smelting there is obtained an iron silicate melt containing approximately 60-90 percent by weight iron, calculated as iron(II)-oxide, which melt is granulated or permitted to solidify and then crushed to pieces of a size suitable for charging to a furnace unit for the production of crude iron.

2. A method according to claim 1, characterized in that excess heat generated during the autogenous smelting process is used for smelting iron oxide material.

3. A method according to claim 2, characterized in that the iron oxide material is pyrite cinders.

4. A method according to claim 2, characterized in that the iron oxide material is iron ore concentrates.

5. A method according to claim 2, characterized in that the iron oxide material is slag obtained from a copper plant.

6. A method according to claim 2, characterized in that the iron oxide material is a slag obtained from a lead plant.

7. A method according to claim 1, characterized in that smelting is carried out in a flash smelter.

8. A method according to claim 1, characterized in that the smelting is effected by charging oxygen gas or air enriched in oxygen to said furnace.

9. A method according to claim 1, characterized in that the smelting process is carried out with a residual quantity
of sulphur of such magnitude that copper, nickel and cobalt can form together with sulphur a matte which can be tapped from said furnace.

10. A method according to claim 1, characterized in that the solidified slag is crushed to a size suitable for charging to a blast furnace.
# INTERNATIONAL SEARCH REPORT

**International Application No:** PCT SE78/00018

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all)

According to International Patent Classification (IPC) or to both National Classification and IPC

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II. FIELDS SEARCHED

**Minimum Documentation Searched**

Documented searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched

SE, NO, DK, FI classes as above

III. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
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  - "P" document published prior to the international filing date but on or after the priority date claimed
  - "T" later document published on or after the international filing date or priority date and not in conflict with the application, but cited to understand the principle or theory underlying the invention
  - "X" document of particular relevance

IV. CERTIFICATION

Date of the Actual Completion of the International Search: 1978-10-10

Date of Mailing of this International Search Report: 1978-10-11

Swedish Patent Office

Form PCT/ISA/210 (second sheet) (October 1977)
II. Continuation classification system.
US classification: 75: 23, 24, 29, 30, 40

V. OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:
1. □ Claim numbers ..........., because they relate to subject matter not required to be searched by this Authority, namely:

2. □ Claim numbers ..........., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

VI. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING

This International Searching Authority found multiple inventions in this international application as follows:

1. □ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2. □ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3. □ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

Remark on Protest:
□ The additional search fees were accompanied by applicant's protest.
□ No protest accompanied the payment of additional search fees.